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MODIFICATION OF THE PHASE COMPOSITION OF GLASS BATCH IN GRANULATION

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Phase transformations in glass batches in densification are analyzed. A method for the calculation and construction of phase diagrams is proposed that provides a clear representation of the qualitative and quantitative phase modifications related to the physicochemical processes occurring in the glass batch at particular stages of granule formations and makes it possible to actively control these processes for the purpose of obtaining products with prescribed technological properties.

Granulation by pelletizing is a complex process of interaction between the solid (s), liquid (l), and gaseous (g) phases under the effect of centrifugal-gravitational forces, which is one of the methods for converting freely dispersed systems into a bonded-disperse state. The properties, composition, and the interaction between phases to a large extent determine the efficiency of the granulation process.

A specific feature of glass batches is that along with insoluble components (sand, dolomite, lime, kaolin, etc.) they also contain components that are soluble in water and capable of forming crystal hydrates with different water content (soda, potash, sodium sulfate, etc.).

A glass batch in the air-dry state can be regarded as a two-phase disperse system consisting of the solid and gaseous phases whose contents are approximately equal. This batch has maximum friability and dust generation.

A moistened batch arriving to a granulator plate represents a three-phase disperse system (s–l–g) and preserves rather high friability, since it contains mainly strong-bound moisture. A further moistening of the batch during pelletizing leads to the formation of capillary-mobile moisture within the system, whose presence is one of prerequisites for efficient granule formation.

During the densification, at the stage of formation of seed granules with a denser structure, the pore space becomes filled with the liquid phase. The pore solution containing positively and negatively charged ions of dissolved inorganic salts together with the finest disperse phase particles form the pore suspension. The displacement of the pore solution to the granule surface facilitates the adhesion of glass batch particles to the granule and the growth of the latter. At the same time, the concentration of the pore suspension inside the granule grows due to a decreasing liquid phase vo-

lume and evolving crystallization processes accompanied by the formation of a large number of small crystals. As the concentration of the pore suspension grows, the number of contacts per granule volume unit increases, which ensures its dynamic strength.

The gaseous phase that is mainly represented by air is removed from the interparticle space during the granule formation. However, a certain amount of air virtually always persists inside the granule structure, both in a fixed state and in the dissolved form. Thus, the three-phase state of the disperse system persists in the granule as well.

It is known that the growth of granules is limited by the rate of capillary mixture exchange in densification [1]. In this context, the kinetics of capillary moisture exchange in the densification of a disperse system can serve as a physical model of the process of granule formation by pelletizing.

The earlier performed experimental studies of moisture absorption kinetics in glass batch layers of different compositions identified the effect of natural and technological properties of raw materials on the nature and velocity of capillary moisture exchange [2].

The specifics of the kinetics of capillary moisture exchange in pelletizing consists in the fact that a disperse system experiences consolidation under the effect of external forces and at the same time the mobility of the liquid phase is modified. Furthermore, impregnation is accompanied by the dissolution and crystallization of chemically active glass batch components, which changes the ratio between the phases and their qualitative and quantitative compositions.

The present study describes the results of studying the kinetics of capillary moisture exchange in a layer of a disperse material under a constant uniformly distributed load. The experiments were performed on a plant ensuring a uniform moisture supply to the sample surface. The quantity of

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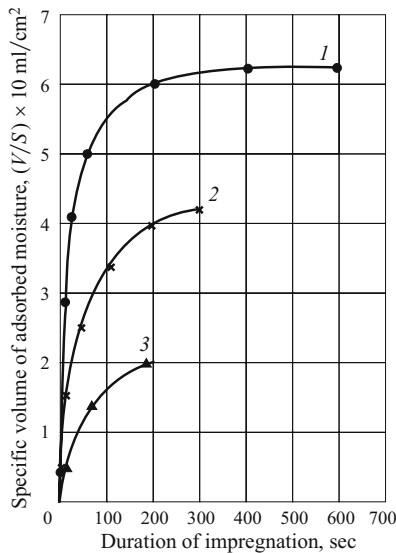


Fig. 1. Kinetics of moisture absorption in model batch: 1) without loading; 2) with loading; 3) with loading at temperature of 40–45°C.

absorbed moisture was controlled via the measuring capillary and by determining the moisture content of an impregnated sample by the drying method. The variation in the height of the sample layer during moistening was registered using the graduation scale on the lateral surface of an organic glass cartridge. The inner diameter of the cartridge was 12 mm, the material layer height was 50 mm, and the constant uniformly distributed load was 0.5 MPa. The end of impregnation was estimated based on the moistening of the upper layer of the sample. The experiments were performed using a model batch that was a mixture of sand, soda, and kolin in the ratio of 75 : 20 : 5 (wt.%). The results of the experiments are shown in Fig. 1.

The kinetic curves have three typical segments differing in their moisture absorption rate. The intensity of the transition of a system from one state to another at particular stages of moistening, mostly related to the processes of dissolution and crystallization of soda, sufficiently fully reflects the coefficient of capillary impregnation velocity K_{ci} , which is determined as the slope of tangent line to certain segments of the kinetic curve. The final points at the curves correspond to the water-saturated state of the sample, i.e., to the end of impregnation.

When moistening samples in the ordinary conditions (without loading), the time of reaching the water-saturated state and the volume of absorbed moisture have maximal values. The moisture absorption intensity ($K_{ci} = 0.12$) corresponding to the first stage of impregnation decreases after passing to the second state and reaches its minimum value ($K_{ci} = 0.05$) at the final stage of impregnation. The volume of absorbed moisture and the time of reaching the water-saturated state become 1.5–2 times lower when samples are impregnated under a constant uniformly distributed load, which is related to a decreased pore size and an increase capillary

potential. The intensity of moisture absorption increases under loaded moistening of samples prepared from a batch preheated to a temperature of 45–50°C, which is due to an increased solubility of soda and its decreased crystallization activity. It is known that moistened soda at a temperature above 45°C contains only anhydrous sodium carbonate and its monohydrate [3].

The present work continues the study in [4], which experimentally established a correlation between moisture absorption kinetics and the phase transformation in moistened glass batch at certain stages of the granulation process.

However, to control the formation of granules, one needs parameters that would take into account the qualitative and quantitative modifications of the phase composition at all process stages. For this purpose, we used the law of the constancy of the volumetric phase composition of disperse systems, which states that the sum of the volumetric contents of the solid, liquid, and gaseous phases of a system is a constant value at any time moment, regardless of structural type, the technological stage, and the type of energy impact on the system [5]. Certain modifications were introduced into the existing method for calculating the volumetric contents of the phases, allowing one to take into account the effect of the dissolution and crystallization of chemically active components on phase transformations during impregnation.

It is known that a batch in the air-dry state constitutes a two-phase system consisting of the solid and gaseous phases, for which the law of the constancy of the phase composition reads as follows:

$$K_s + K_g = 1,$$

where K_s and K_g are the volumetric contents of the solid and gaseous phases in the batch before moistening.

During moistening, the disperse system passes into the three-phase state (s : 1 : g), whereas the law of constancy holds for any stage of moistening:

$$K_{si} + K_{li} + K_{gi} = 1,$$

where K_{si} , K_{li} , and K_{gi} are the volumetric contents of the solid, liquid, and gaseous phases in the system at the i th stage of impregnation; $i = 1, 2, \dots, n$ (n is the number of stages).

It is proposed to calculate the volumetric content of the solid phase using the formula

$$K_{si} = \rho_{si} / \rho_{ti},$$

where ρ_{si} is the apparent density of the dry material layer, g/cm^3 ; ρ_{ti} is the true density of the material at the i th impregnation stage, g/cm^3 .

The apparent density was calculated from the formula

$$\rho_{si} = \rho_{mi} / (1 + W_i),$$

where ρ_{mi} is the apparent density of moist material at the i th stage of impregnation, g/cm^3 and W_i is the absolute moisture of material at the i th stage of impregnation, rel. units.

The absolute moisture of the impregnated sample was determined by the drying method and W_i values were calculated specifying the condition of a uniform moisture distribution in the sample volume.

The true density of the solid phase ρ_{ti} changes during impregnation, on the one hand, due to the partial or full dissolution of individual soda grains and, on the other hand, due to the formation of crystal hydrates of a different water content and density,

The true density of the solid phase at the respective impregnation stage is found from the formula

$$\rho_{ti} = \sum_{j=1}^m V_j \rho_j,$$

where V_j is the volumetric part of the j th phase, rel. units; ρ_j is the density of the j th phase, g/cm^3 ; m is the number of phases.

To determine the volumetric parts of the phases at the respective stage of impregnation, the qualitative and quantitative x-ray phase analysis of soda was performed in the air-dry state and then 2, 5, and 10 min after the start of moistening. The results of processing the obtained diffraction patterns based on the comparison between the total integral intensities of all diffraction reflections of each phase are shown in Table 1.

The volumetric content of the liquid phase was calculated from the formula

$$K_{li} = (\rho_{si}/\rho_{li})W_i,$$

where ρ_{li} is the liquid phase density at the i th state of impregnation, g/cm^3 .

The density of the liquid phase constituting a soda solution varied from 1.01 to 1.20 g/cm^3 during moistening depending on the solution concentration. The density of the liquid phase was calculated from the formula

$$\rho_{li} = \frac{1}{C_{fi} - C_{bi}} \int_{C_{bi}}^{C_{fi}} \rho_i(C) dC,$$

where C_{bi} and C_{fi} are the initial and final concentrations of the liquid phase at the corresponding stage of impregnation, g/cm^3 .

The volumetric content of the gaseous phase was found from the expression

$$K_{gi} = 1 - K_{si} - K_{li}.$$

Particular technological stages in the granulation processes corresponding to different impregnation stages can be represented in the form of a phase diagram based on the data given in Table 2. This diagram is based on an equilateral triangle

TABLE 1

Sample	Volumetric content of phases, %				
	Na_2CO_3	NaHCO_3	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	$\text{Na}_2\text{CO}_3 \cdot 2.5\text{H}_2\text{O}$	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
In air-dry state	66	32	2	—	—
After moistening in, min:					
2	46	—	28	10	16
5	44	—	35	7	14
10	40	—	43	5	12

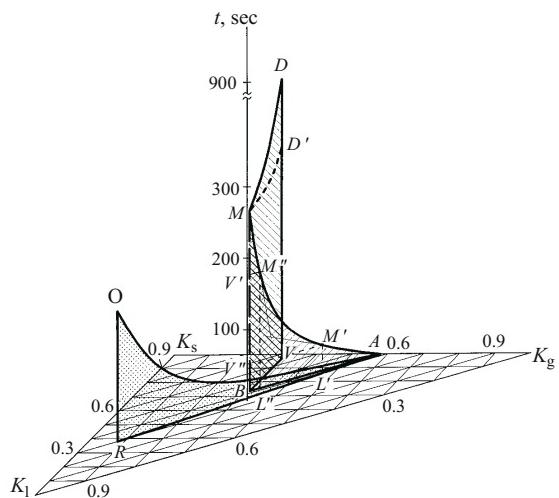


Fig. 2. Phase characteristics of model batch.

whose sides indicate variations in the contents of the solid, liquid, and gaseous phases from 0 to 1 (Fig. 2).

The time axis is positioned in the center of the triangle. The phase composition of the batch ($K_s = 0.412$, $K_g = 0.588$) at the beginning of sintering corresponds to the point A on the line $K_s - K_g$. The variation in the phase composition during moistening proceeds according to the line AB . The point B corresponds to the water-saturated state of the sample in the end of the impregnation ($K_{si} = 0.465$, $K_{li} = 0.318$, $K_{gi} = 0.217$), which occurs 270–280 sec after the beginning of moisture absorption (point M). For any point lying on the line AB it is possible to determine the phase composition of the disperse system and the duration of its existence and, vice versa, the phase composition of the disperse system can be found for any time moment after the beginning of moistening. Of special interest is the segment $L'L''$ corresponding to the phase transformations related to the beginning of crystallization processes in the disperse system. As can be seen from the diagram, these phase transformations take place within 120–130 sec (segment $V'V''$).

The impregnation of samples at 45–50°C is accompanied by an increasing volume of moisture absorbed and a growing water absorption rate. For this particular case the variation of the phase composition occurs along the line AR and the water-saturated state of the sample occurs 200–210 sec after the beginning of impregnation (point O).

TABLE 2

Impregnation duration, sec	W_i	ρ_{mi} , g/cm ³	ρ_{dri} , g/cm ³	K_{si}	K_{li}	K_{gi}
0	0	—	1.29	0.412	0	0.588
15	4.89	1.36	1.30	0.425	0.052	0.523
38	7.34	1.43	1.33	0.436	0.081	0.483
67	9.79	1.47	1.34	0.447	0.109	0.444
95	12.24	1.51	1.35	0.450	0.138	0.412
140	16.68	1.56	1.36	0.462	0.349	0.189
220	17.13	1.60	1.37	0.465	0.339	0.196
270	19.02	1.63	1.37	0.465	0.318	0.217

Furthermore, the study of drying of impregnated samples at various temperatures indicated that to reach a prescribed phase composition, for instance, the one corresponding to the point V , we need 800–850 sec (point D) at the drying temperature of 200°C or 400–450 sec (point D') at the temperature of 400°C. The phase modifications occurring in the system in this case correspond to the line BV .

Thus, the proposed method for the calculation and construction of the phase diagram gives a clear representation of the qualitative and quantitative phase transformations related

to the physicochemical processes occurring in the glass batch at certain stages of the granulation process and makes it possible to plan the ways for actively controlling these processes, for instance, modifying the quantity and temperature of water at the stage of batch moistening, the duration of contact between phases, the heat treatment regime, etc., which provides for a product with preset technological properties.

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